

METHOD 9210A

POTENTIOMETRIC DETERMINATION OF NITRATE IN AQUEOUS SAMPLES WITH AN ION-SELECTIVE ELECTRODE

1.0 SCOPE AND APPLICATION

1.1 This method may be used for measuring solubilized nitrate in drinking waters, natural surface waters, groundwaters, domestic and industrial wastewaters, and in soil extracts (ASTM Standards D 4646-87, D 5233-92 or D 3987-85).

NOTE: This method is for the analysis of simple (non-complexed) nitrate ion rather than total nitrate, because the analysis using the ion-selective electrode is not preceded by a distillation step.

1.2 A method detection limit (MDL) of 2.0 mg/L has been calculated. A linear calibration ($\pm 20\%$ RSD) can be obtained over the range of 5.0 to 200 (mg/L). Results less than 5.0 mg/L will be biased high while results greater than 200 mg/L will be biased low.

1.3 Ion-selective electrodes (ISEs) must be used carefully, and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results, therefore, requires some knowledge of the sample composition.

NOTE: ISE manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

2.0 SUMMARY OF METHOD

2.1 Solubilized nitrate is determined potentiometrically using a nitrate ion-selective electrode (ISE) in conjunction with a double-junction reference electrode and a pH meter with an expanded millivolt scale (mV), or an ISE meter capable of being calibrated directly in terms of nitrate concentration.

2.2 Standards and samples are mixed 50:1 (v/v) with an ionic strength adjustment solution. Calibration is performed by analyzing a series of standards and plotting mV vs. nitrate-nitrogen concentration on semilog paper, or by calibrating the ion meter directly in terms of nitrate concentration.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for applicable definitions.

4.0 INTERFERENCES

4.1 The nitrate electrode responds to numerous interfering anions. Most of the interferants, however, can be rendered harmless by adding suitable reagents. Cyanide, bisulfide, bicarbonate, carbonate, and phosphate are removed by adjusting the solution to pH 4 with boric acid. Chloride, bromide, and iodide are removed by adding silver sulfate solution. Nitrite is also an interferent, as shown in Table 1, and can be removed by adding sulfamic acid. The amounts of silver sulfate and sulfamic acid needed will vary based on the concentrations of interferants. As a general guide, 1 mL of silver sulfate will eliminate chloride interference in a 50-mL sample containing 35 mg/L Cl^- . 1 mL of sulfamic acid solution will eliminate nitrite interference in a 50-mL sample containing 95 mg/L NO_2^- .

4.2 Temperature changes affect electrode potentials. Using an ISE calibrated at 22°C, a 20.0 mg/L nitrate solution was measured as 20.6 mg/L at 22°C and 12.9 mg/L at 32°C (see Ref. 2). Therefore, standards and samples must be equilibrated at the same temperature ($\pm 1^\circ\text{C}$).

4.3 The user should be aware of the potential for interferences from colloidal substances and that, if necessary, the samples should be filtered. If the samples are filtered, the associated method blanks must also be filtered.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

6.1 pH/mV meter - capable of reading to 0.1 mV, may be automated.

6.2 Nitrate ISE and double-junction reference electrode.

6.3 Thermally-isolated magnetic stirrer, polytetrafluoroethylene (PTFE)-coated stir bar, and stopwatch.

6.4 Volumetric flask - Class A, 100-mL.

6.5 Analytical balance - capable of accuracy to 0.001g.

7.0 REAGENTS

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades

may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water - all references to water in this method refer to reagent water, as defined in Chapter One.

7.3 Ionic strength adjustor (ISA) solution (2 M, $(\text{NH}_4)_2\text{SO}_4$) - dissolve 26.4 g of ammonium sulfate in a 100-mL Class A volumetric flask and make to volume with reagent water.

7.4 Boric acid (1 M, H_3BO_3) solution - dissolve 6.2 g of boric acid in a 100-mL Class A volumetric flask and make to volume with reagent water. This is the preservative solution for numerous anions and bacteria.

7.5 Silver sulfate (0.05 M, Ag_2SO_4) solution - to remove interferences, as noted in Section 4.1. Dissolve 1.6 g of silver sulfate in a 100-mL volumetric flask and make to volume with reagent water. A saturated silver sulfate solution contains approximately 5.5 g/L of solubilized silver.

7.6 Sulfamic acid (0.1 M, HOSO_2NH_2) solution - to remove nitrite from sample, as noted in Section 4.1. Dissolve 0.97 g of sulfamic acid in a 100-mL volumetric flask and make to volume with reagent water.

7.7 Nitrate calibration stock solution (1,000 mg/L, NO_3^- -N) - dissolve 7.218 g of potassium nitrate (dried for two hours at 110°C and stored in a desiccator) in reagent water and dilute to 1 L in a volumetric flask. Store in a clean bottle. This standard may also be purchased from a vendor.

7.8 Nitrate calibration standards - prepare a series of calibration standards by diluting the 1,000 mg/L nitrate standard. A suitable series is given in the table below. These standards should be replaced daily.

Volume of 1,000 mg/L NO_3^- Solution (mL)	Concentration when Diluted to 50.0 mL (mg/L NO_3^- -N)
0.0500	1.00
0.150	3.00
0.500	10.0
1.50	30.0
5.00	100.0

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

8.2 In most environmental samples, nitrate is not affected by complexation, precipitation, inorganic oxidation-reduction reactions, and protonation. However, in the presence of a reducing agent (e.g., organic matter), bacteria will utilize nitrate as an oxidant, causing a slow decrease in

the nitrate concentration. This potential interference can be obviated by using a preservative. Therefore, samples must be preserved by adding 1 mL of 1M boric acid solution per 100 mL of sample at the time of sampling.

8.3 Samples should be stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

8.4 Samples should be analyzed within 48 hours of collection.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance protocols. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial calibration verification standard (ICV)

After performing the calibration step (Sec. 10.1), verify calibration by analyzing an ICV. The ICV contains a known nitrate concentration at the mid-range of the calibration standards and must be from an independent source. ICV recovery must be 90 - 110 percent. If not, the source of error must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

9.3 Continuing calibration verification standard (CCV)

A CCV must be analyzed after every 10 samples and after the final sample. The CCV contains a known nitrate concentration at the mid-range of the calibration standards and is made from the same source as the calibration curve. The CCV recovery must be 90 - 110 percent. If not, the error source must be found and corrected. If ISE calibration has changed, then all samples analyzed since the last acceptable CCV must be reanalyzed.

9.4 Method blank

A method blank must be analyzed after the ICV and after every CCV. A method blank is a 1% solution of preservative solution in reagent water, mixed 50:1 with the ISA. The result for the method blank must be <1 mg/L nitrate. If not, then the contamination source must be found and corrected. All samples analyzed since the last acceptable method blank must be reanalyzed. If the samples are filtered, then the method blanks must also be filtered.

9.5 Matrix spike/matrix spike duplicate (MS/MSD)

For each batch of samples processed, at least one MS/MSD pair must be carried through the entire sample preparation and analytical process. The MS/MSD are intra-laboratory split samples, spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Refer to the definitions of bias and precision, in Chapter One, for the proper data reduction protocols. MS/MSD samples should be spiked at the project-specific action level or, when lacking project-specific action levels, between the low- and mid-level standards.

Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses. In the absence of historical data, this accuracy limit should be set at $\pm 20\%$ of the spiked value and the precision limit should be set at ≤ 20 relative percent difference (RPD). Acceptance limits derived from historical data must be no wider than $\pm 20\%$. Refer to Sec. 4.4.2 of Chapter One for guidance. If the bias and precision indicators are outside the laboratory control limits or if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, an interference should be suspected (refer to Section 4.0).

10.0 CALIBRATION AND STANDARDIZATION

10.1 When using a nitrate ISE and a separate double-junction reference electrode, ensure that reference electrode inner and outer chambers are filled with solutions recommended by the manufacturer. Equilibrate the electrodes for at least one hour in a 100 mg/L nitrate standard before use.

10.2 Calibrate the nitrate ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 3.00 mg/L and 30.0 mg/L nitrate standards. Add 50.0 mL of standard, 0.50 mL of preservative solution, and 1.00 mL of ISA to a 100-mL beaker. Add a PTFE-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of nitrate concentration by following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of nitrate concentration. The slope must be 54-60 mV per decade of nitrate concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual.

11.0 PROCEDURE

11.1 Allow samples and standards to equilibrate to room temperature.

11.2 Prior to and between analyses, rinse the electrodes thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed for five minutes in reagent water.

11.3 Add 50.0 mL of sample and 1.00 mL of ISA to a 100-mL beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. If reading mV, determine nitrate-nitrogen concentration from the calibration curve.

11.4 When analyses have been completed, rinse the electrodes thoroughly with water and store them in a 100 mg/L nitrate standard solution. If the electrodes will not be used again for more than one day, drain the reference electrode internal filling solutions, rinse with reagent water, and store dry or store according to the manufacturer's instructions.

12.0 DATA ANALYSIS AND CALCULATIONS

Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 In a single-laboratory evaluation, a series of standards with known nitrate concentrations was analyzed with a nitrate ISE. Measurements were obtained over three consecutive days using an Orion 9307 nitrate ISE and an Orion 9002 double-junction reference electrode connected to an Orion 940 ISE meter. A two-point calibration (5.00 and 50.0 mg/L nitrate) was performed prior to analysis. The results are listed in Table 2.

13.2 In the same study, three groundwater samples were spiked with nitrate at four different concentrations and measured with the nitrate ISE. The groundwater samples initially contained <0.1 to 2.3 mg/L nitrate. Each spiked sample was analyzed at each concentration, and the mean recoveries and RSDs are given in Table 3.

13.3 A 50-g portion of soil, which initially contained 0.7 mg/kg nitrate, was spiked with 25.0 mg/kg of nitrate to obtain an anion concentration in a single extract volume within the linear range of the ISE. The extract was then analyzed for nitrate using this ISE method, and 89% of the soil spike was recovered (Ref. 3).

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society available from the American Chemical Society, 1155 16th Street NW, Washington DC, 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management,

consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society.

16.0 REFERENCES

1. Model 93-07 Nitrate Electrode Instruction Manual. Orion Research, Inc., Boston, MA, 1986.
2. Miller, E. L., Waltman, D. W., and Hillman, D. C., "Single-Laboratory Evaluation of Fluoride, Chloride, Bromide, Cyanide, and Nitrate Ion-Selective Electrodes for Use in SW-846 Methods," Lockheed Engineering and Sciences Company for Environmental Monitoring Systems Laboratory, U.S. EPA, EPA/600/X-90/221, September 1990.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 3 and a flow diagram of the method procedure.

TABLE 1
NITRATE ISE INTERFERENCES

Interference	Conc. (mg/L)	Measured Nitrate Conc. (mg/L)	RSD (%)
None	25.0	26	6.2
0.01 M H ₂ SO ₄	25.0	24.5	5.9
100 mg/L NO ₂ ⁻	25.0	46	9.1
100 mg/L NO ₂ ⁻ + 500 mg/L HOSO ₂ NH ₂	25.0	26	6.3

Data taken from Reference 1.

TABLE 2

EXAMPLE RESULTS FROM A SINGLE-LABORATORY ACCURACY EVALUATION
OF A NITRATE ISE

Nitrate Conc. (mg/L)	Nitrate Detected (mg/L)	Recovery (%)	RSD (%)
0.100	1.01	1010	53
0.200	1.04	520	17
0.500	1.23	246	8
1.00	1.71	171	2
2.00	2.45	123	7
5.00	5.0	100	0
10.0	11.0	110	8
20.0	18.9	95	14
50.0	50	100	1
100	96	96	13
200	164	82	3
400	310	77	8
1000	480	48	17

Data taken from Reference 1 and are for illustrative purposes only.

TABLE 3

EXAMPLE SPIKE RECOVERIES OF NITRATE IN THREE GROUNDWATER SAMPLES

Spike Conc. (mg/L)	Recovery (%)	RSD (%)
2.00	113	10.7
3.00	106	7.6
5.00	98	1.2
10.0	89	2.7

Data taken from Reference 2 and are for illustrative purposes only.

METHOD 9210A

POTENTIOMETRIC DETERMINATION OF NITRATE IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

